

Electrochemical properties of aluminium anodes for Al/air batteries with aqueous sodium chloride electrolyte

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Received: 7 March 2012 / Accepted: 22 July 2012 / Published online: 3 August 2012
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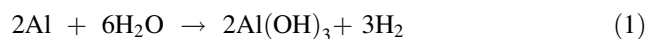
Abstract In order to develop the new anode materials for Al/air batteries, electrochemical properties of pure aluminium (99.999 %), technical grade aluminium (99.8 %) and the alloys with indium and tin, i.e. Al—0.1 % In, Al—0.2 % Sn and Al—0.1 % In—0.2 % Sn have been investigated in 2 mol dm⁻³ NaCl solution. The aluminium materials were polarized anodically in the range 20–100 mA cm⁻² for a 30 min period. During the anodic polarization variation in potential was recorded as a function of time and the simultaneous hydrogen evolution was measured. The rate of hydrogen evolution reaction was found to increase with increasing anodic polarization which is characteristic of the negative difference effect. The additional information concerning the corrosion behaviour of the tested materials was provided by light microscope imaging. The results show that the examined technical grade aluminium alloys could serve as suitable anodes for Al/air batteries containing sodium chloride electrolyte; with Al–In exhibiting the most remarkable characteristics. The addition of In as alloying component to aluminium reduces electrode polarization,

decreases hydrogen evolution rate and increases the anode efficiency.

Keywords Aluminium · Aluminium alloys · Anodic polarization · Negative difference effect

1 Introduction

Aluminium-air technology has been investigated for several decades [1]. To a significant extent, the performance of an aluminium/air battery is determined by the electrochemical and corrosion properties of the aluminium alloy electrode [2]. It is well known that aluminium is passivated in air or in aqueous solutions by formation of a thin compact oxide layer of several nm thicknesses [3]. The oxide layer on the aluminium surface however is detrimental to battery performance, restricting the ability to achieve the reversible potential and causing delayed activation of the anode [4]. Another setback with aluminium and its alloys is related to corrosion and the associated hydrogen gas evolution:



It has been demonstrated that suppression of the parasitic corrosion while maintaining the electrode activity of the anode metal can be achieved in part using high-purity aluminium or by employing aluminium-based anode materials with minor additions of indium, gallium, zinc, magnesium, tin and thallium [2–17]. The need to use high-purity aluminium or high-purity aluminium-based alloys results in a significant increase in the cost of the anode, and thus an increase in the total cost of energy generated by the aluminium/air battery, which narrows the range of possible applications for this type of power source [18].

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The present study builds on our previous efforts on the electrochemical study of pure aluminium, technical grade aluminium and some alloys namely, Al–In, Al–Sn, and Al–In–Sn as anodes for aluminium/air battery with sodium chloride electrolyte. The aluminium materials were analysed by galvanostatic anodic polarization tests to establish their anode efficiency and their corrosion behaviour. For this purpose during the galvanostatic test the simultaneous hydrogen evolution was measured as a function of time. Additional information on the corrosion behaviour of the tested materials was provided by light microscope imaging.

In addition, the negative difference effect (NDE) (which means the increase of the hydrogen evolution by increasing the applied current) [5, 11] was verified for the studied Al anodes.

Several models have been suggested to explain the negative difference effect [5]. These include occurrence of uncommon valency; breakdown of the protective film and as well as disintegration of the metal surface (chunk effect).

According to the uncommon valency effect, the aluminium dissolution reaction is assisted by chloride ions and takes place in three consecutive one-electron transfer steps, with the third of these being the rate determining step in the electrode kinetic sequence [19]. Monovalent aluminium ions occur, i.e. Al^+ , which are unstable and immediately oxidize to Al^{3+} ions. Oxidation takes place partly in the electrical double layer, and partly by chemical transformation. The chemical reaction involves H^+ ions or water molecules, whereby hydrogen is formed in the solution near the electrode surface. Increasing the anodic current increases the concentration of Al^+ ions as well as the chemical oxidation rate. The apparent lower valence observed experimentally during anodic dissolution of aluminium (anomalous valence effect) has been attributed to the formation of species of lower valence than usually obtained. This effect has been observed during anodic dissolution of Al, Mn, Be, Ga, Tl, In, Cd, Cu, Fe, Mg, Zn and has been extensively reviewed by James [20], and has been related to mechanical disintegration of the metal, lower intermediate valence (e.g., Al^+ , Mg^+ , etc.) and chemical disproportionation of such ions, as well as reaction of the lower valence ions with solvent molecules.

The film breakdown model was proposed to account for the anomalous anodic behaviour of metals as manifested by the decreased current efficiencies and negative difference effects and is often encountered during the dissolution of Mg, Zn and Al. Various versions of this model can be found, most of them are based on the fact that these metals during anodic dissolution are covered with a passive film which is ruptured and occasionally repaired. Again, depending on the composition of the electrolyte, some of its constituents, (e.g., Cl^- ions), modify the properties of

the film. These processes are often associated with pitting and the increase in steady-state porosity should normally lead to an increased rate of hydrogen evolution on the bare parts of the metal.

The chunk effect attributes the lower apparent valence resulting from the anomalous dissolution of Zn and Al—to mechanical disintegration [21]. According to this mechanism, the anodic current in some way undercuts groups of atoms on the surface which, as metallic particles stay loosely attached to the surface or are transported hydrodynamically into the bulk. If the electrolyte is aggressive to the metal, i.e. H_2SO_4 or HCl , spontaneous corrosion of such particles in the electrolyte is to be expected, resulting in the accumulation of metallic ions in the solution at a higher rate than corresponds to the amount of current passed, and also, additional hydrogen evolution.

Due to the low environmental impact of the aluminium corrosion in neutral electrolyte, it is very interesting not only for application in specific and confined fields but also for energy conversion systems [18, 22, 23]. In fact, the reaction produces aluminium hydroxide [$\text{Al}(\text{OH})_3$] and hydrogen along with a significant amount of heat. In addition, this reaction can be achieved under mild conditions of temperature and pressure. The aluminium hydroxide by-product can be recycled back to aluminium and also the indium and tin components are recoverable. Again, although the hydrogen evolution reaction is an undesirable secondary reaction in Al/air batteries, this reaction provides a compact source of hydrogen which may be employed in a variety of fuel cells or H_2 -fuelled internal combustion engines [22]. Accordingly, further studies on applicability of examined technical grade aluminium alloys as anodes in Al/air battery for combined production of electrical power and hydrogen must be done. Such work is underway in our laboratory.

2 Experimental

Measurements were made on pure aluminium (99.999 wt%) [Al(5N)], technical grade aluminium (99.8 wt%) [Al(tech.)] and its alloys namely Al–0.1 wt% In (Al–In), Al–0.2 wt% Sn (Al–Sn), Al–0.1 wt% In–0.2 wt% Sn (Al–In–Sn). All alloys were prepared from aluminium of purity 99.8 %, with high-purity (99.999 %) indium and/or tin as alloying additions. After alloying, the alloy was homogenized at 800–850 °C for 15 min and then quenched with cold water.

The specimens were encapsulated in epoxy resin with only a circular flat face (0.5 cm² area) exposed to the solution. Before measurements the samples were abraded with successively finer grades of emery paper, rinsed with doubly distilled water and immersed for 1 min in 0.1 mol dm^{−3} NaOH at 40 °C to remove the air-formed

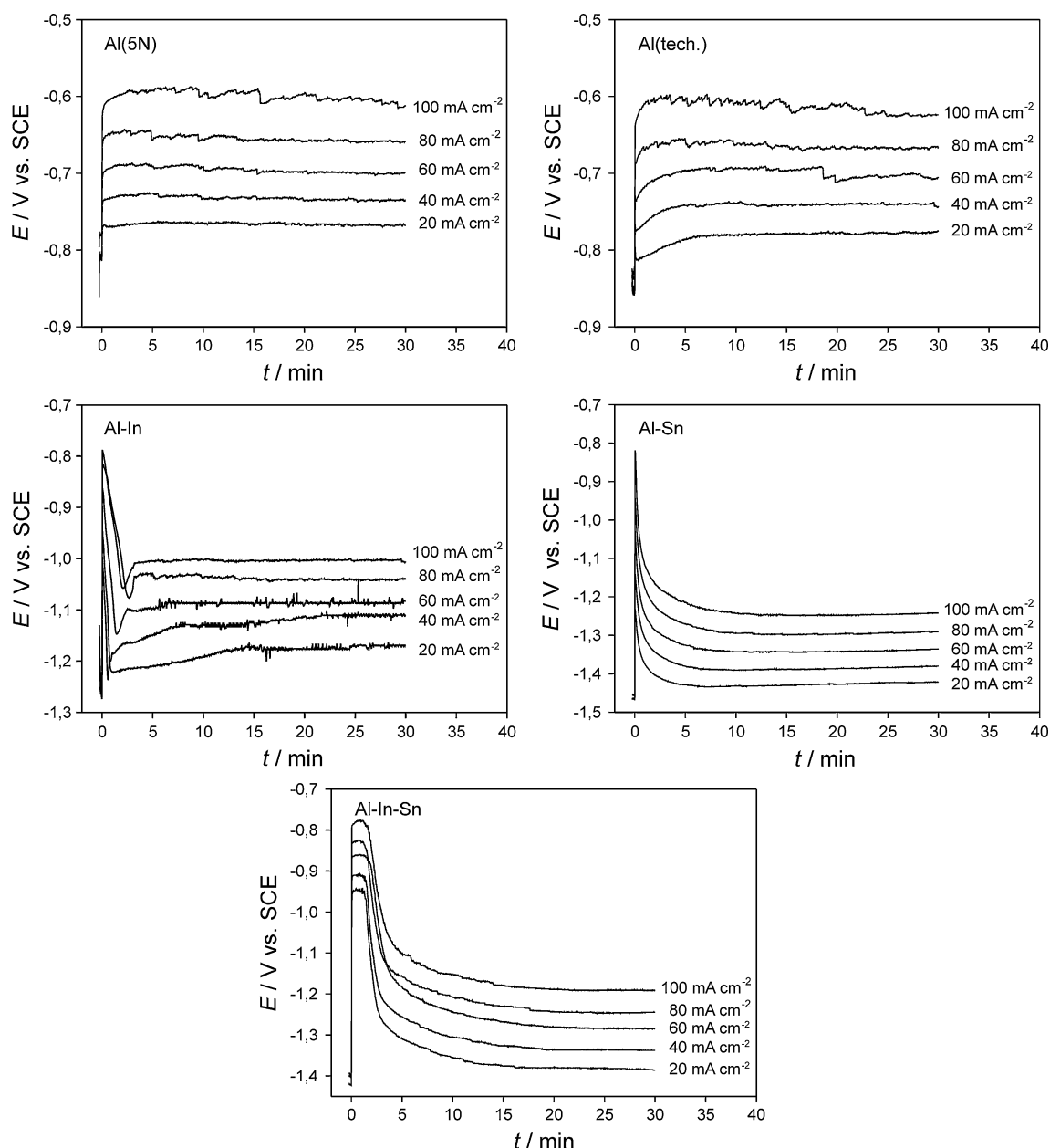


Fig. 1 Potential-time responses recorded for Al(5N), Al(tech.), Al-In, Al-Sn and Al-In-Sn alloys in 2 mol dm^{-3} NaCl solution and at different current densities

oxide layer from their surface. Afterwards the electrodes were rinsed in doubly distilled water and placed in the closed Pyrex glass cell for electrochemical measurement, as well as volumetric measurement of evolved hydrogen gas. The details of the hydrogen collecting system have been described in a previous study [16].

The counter electrode was a platinum sheet and the reference electrode was a saturated calomel electrode (SCE). The electrolyte, 2 mol dm^{-3} NaCl solution, was prepared using deionised water from a TKA water purification system and analytical grade sodium chloride from Sigma-Aldrich.

The volume of the solution used in the tests was always 250 ml. All measurements were carried at $25 \pm 0.1^\circ\text{C}$.

The galvanostatic tests were carried out by imposing anodic current density in the range $20\text{--}100 \text{ mA cm}^{-2}$ on samples during a 30 min period. During the anodic polarization variation in potential was recorded as a function of time and the simultaneous hydrogen evolution was measured. After polarization tests, samples were washed, dried and the surface of Al and Al-alloys was observed by an optical microscope Citoval (Carl Zeiss Jena) at a magnification of 100 times.

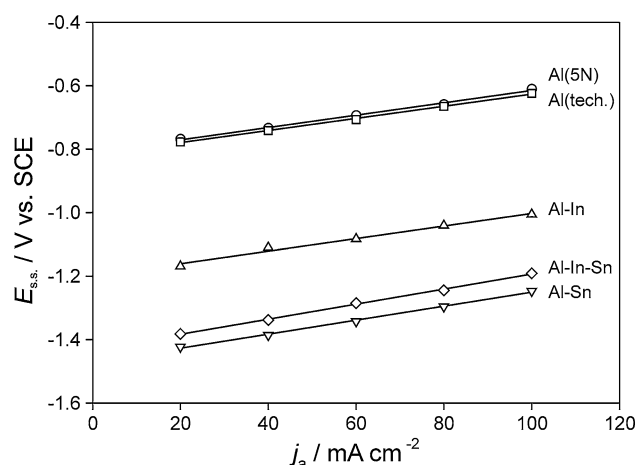


Fig. 2 Dependence of steady state potential ($E_{s.s.}$) on the anodic current density for Al(5N), Al(tech.), Al-In, Al-Sn and Al-In-Sn alloys in 2 mol dm⁻³ NaCl solution

All the electrochemical experiments were undertaken using a computer-controlled with an EG&G PAR model 273A potentiostat/galvanostat.

3 Results and discussion

3.1 Galvanostatic anodic polarization

Figure 1 shows the potential-time response of Al(5N), Al(tech.), Al-In, Al-Sn and Al-In-Sn electrodes in 2 mol dm⁻³ NaCl solution under galvanostatic anodic polarization conditions in the range 20–100 mA cm⁻². The potential of the aluminium samples can be seen to increase initially before attaining steady values. The initial part represents a typical galvanostatic charging curve with the initial jump due to the pseudo-ohmic resistance and a subsequent charging of interfacial capacitance [24, 25]. Galvanostatic charging occurs in a time scale of few milliseconds in the mA cm⁻² region [24, 25]. After charging is ended, potential continues to increase almost linearly before attaining a steady value, i.e. to the potential plateau of active anodic dissolution [24, 25]. In the case of Al-alloys, potential increases up to a certain maximum value and then decreases to the potential plateau of active anodic dissolution [24, 25]. All of these observations are consistent with the reported results of potentiodynamic and impedance measurements [16, 17], i.e. the Al-materials remain active throughout the examined anodic current range.

The steady state potential of all samples increased linearly with anodic current (Fig. 2). Impurities present in technical grade aluminium affect the OCP and the corrosion behaviour [25], while they have little effect on the potential plateau of

active dissolution, i.e. the stable state potential of Al(5N) and Al(tech.) differ by approximately 35 mV (Figs. 1, 2). The addition of alloying components to aluminium produced in all cases a considerable shift of the steady state potential towards the negative direction. The Al-In alloy exhibits potential of about 0.40 V more negative than that of aluminium in the same solution, while that of Al-Sn was about 0.6 V more negative. The behaviour of the Al-In-Sn alloy is more or less similar to that of Al-Sn alloy and steady state value is approximately 0.65 V more negative than that observed for aluminium. The presence of In and/or Sn as alloying components in aluminium enhances Cl⁻ ion adsorption at high negative potentials, leading to dissolution of the alloy [26]. Therefore, the active dissolution of the alloys occur at much lower electrode polarization so that the polarization of the examined electrodes decreased in the order; Al(5N) > Al(tech.) > Al-In > Al-In-Sn > Al-Sn.

Hydrogen gas evolution was simultaneously measured as a function of time during the galvanostatic test and the results are presented in Fig. 3. At all current densities examined, the hydrogen evolution rate increase with time in the order Al-In < Al(5N) < Al(tech.) < Al-In-Sn < Al-Sn. The rate of hydrogen gas release was used to calculate the current density (j_{H_2}) as follows:

$$j_{H_2} = \frac{zF}{t} \cdot \frac{V}{V_m} \quad (2)$$

where V is the volume of released hydrogen, V_m is the molar volume of gas, z is the number of electrons involved in the reaction, F the Faraday constant, and t is the time.

When examined aluminium samples are anodically polarized in halide solution the rate of hydrogen evolution (expressed in terms of equivalent current density) linearly increases with increasing anodic current density as shown in Fig. 4. The presented results show evidence of NDE, which is quite contrary to the expectation that hydrogen evolution should subside at anodic potentials at least remain constant at a constant-potential plateau. The slope $\Delta j_{H_2} / \Delta j_a$, is taken as a measure of the NDE and the obtained results are summarized in Table 1. The Al-In alloy had the lowest NDE among the samples tested while the highest NDE value was obtained for Al-Sn alloy. NDE increased in the following order: Al-In < Al(5N) < Al(tech.) < Al-In-Sn < Al-Sn, which implies that the composition of the aluminium materials and alloying additives have significant influence on the rate of hydrogen evolution and consequently on the NDE. The experimental data obtained are consistent with the data presented in the literature [5, 11].

The NDE is often correlated with localized anodic dissolution of metals since the effect is typically observed for systems where the metal undergoes pitting corrosion. This applies, for example, to aluminium in chloride, bromide

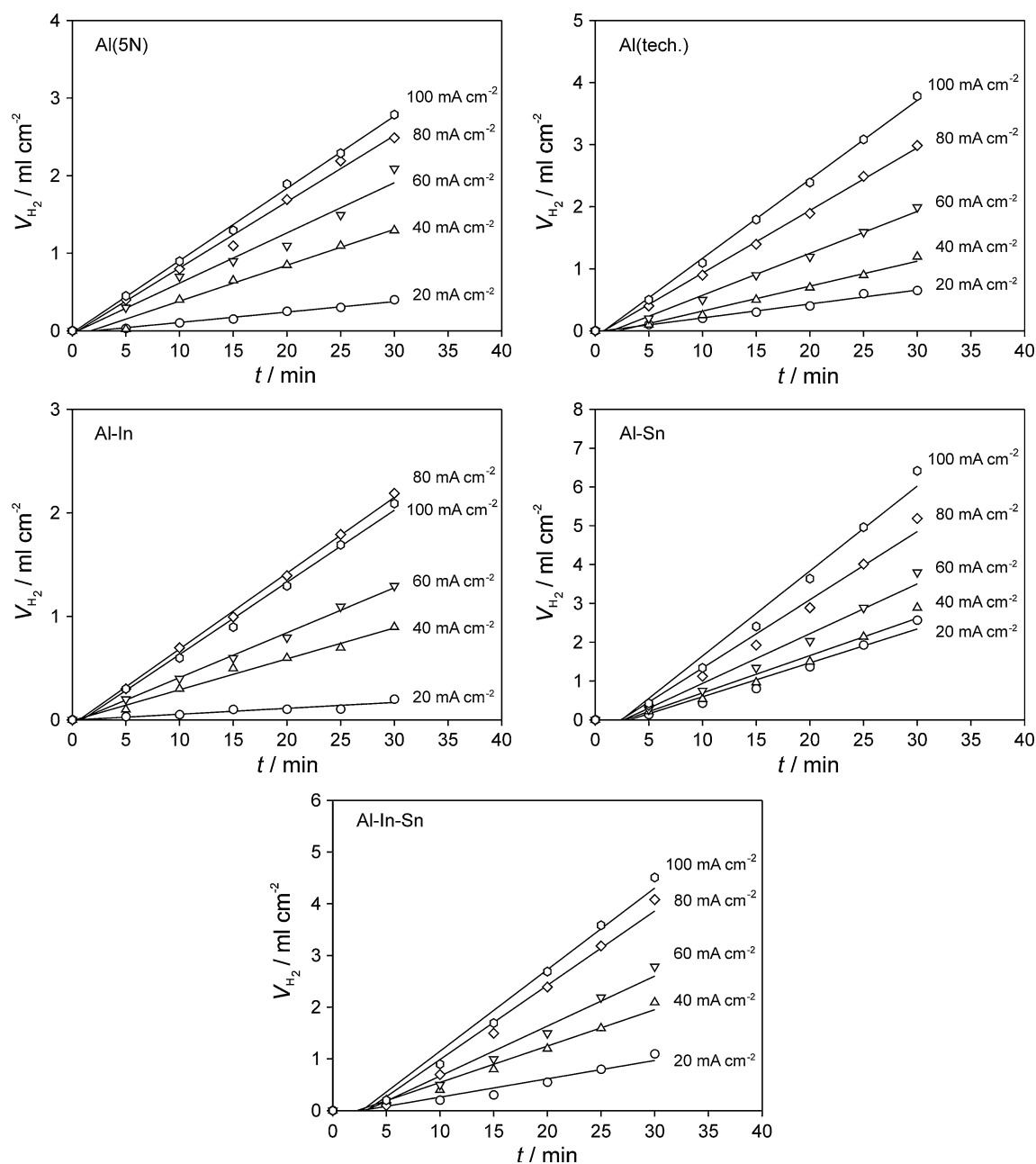
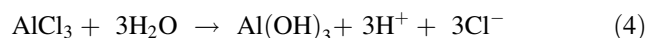
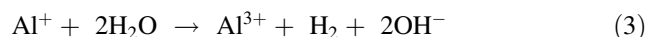


Fig. 3 Hydrogen evolution during galvanostatic tests with Al(5N), Al(tech.), Al-In, Al-Sn and Al-In-Sn alloys in 2 mol dm^{-3} NaCl solution for applied current densities between 20 and 100 mA cm^{-2}

and iodide solutions [11, 27–29]. The generation of hydrogen gas bubbles inside the pits has been confirmed by in situ optical microscopy [30–32]. Hydrogen evolution during anodic polarization is usually explained either by the formation of Al^+ ions and their reaction with H_2O molecules (Eq. 3), or by an increase in acidity at the bottom of the pits due to the hydrolysis reaction of Al^{3+} ions with water containing Cl^- ions (Eq. 4), whereby the pH becomes about 4 and, therefore, the hydrogen evolution reaction is stimulated.



However, the values of the negative difference effect are independent of pH in the range 2–7 [11] showing that hydrogen evolution at large anodic current densities is essentially not as a result of AlCl_3 hydrolysis and local acidification. This is more so if one considers the experimental fact that an Al surface dissolving anodically at ca. 100 mA cm^{-2} in 0.5 mol dm^{-3} NaCl had a shiny surface,

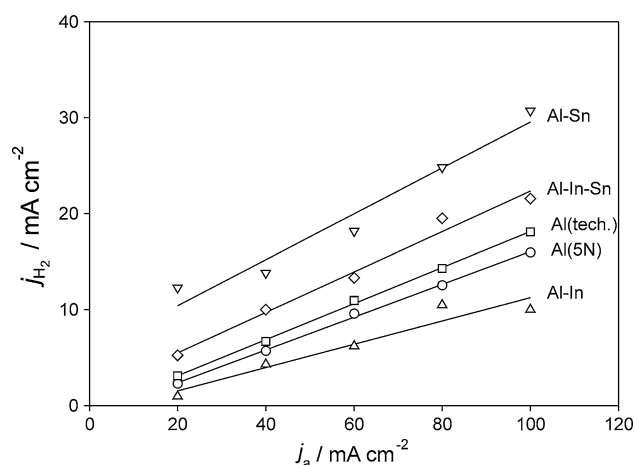


Fig. 4 Rate of hydrogen evolution (expressed in terms of equivalent current density) as a function of the applied anodic current density for Al(5N), Al(tech.), Al–In, Al–Sn and Al–In–Sn alloys in 2 mol dm^{−3} NaCl solution

Table 1 Negative difference effect (NDE) of tested samples in 2 mol dm^{−3} NaCl solution

Sample	NDE
Al(5N)	0.171
Al(tech.)	0.188
Al–In	0.121
Al–Sn	0.235
Al–In–Sn	0.211

with no visible evidence of pitting, as observed at much lower current densities. This is akin to assuming that the entire surface becomes the bottom of a giant pit [5, 33].

The results in this study, however, seem to support occurrence of the uncommon valency model, i.e. constancy of the NDE. The aluminium dissolution reaction is assisted by chloride ion and takes place in three consecutive one-electron transfer steps. Monovalent aluminium ions appear, i.e. Al⁺, which are unstable and so oxidize to Al³⁺ ions. The slower the rate determining step, the more the ionic intermediate will accumulate at the surface and hence, the larger will be its flux through the oxide layer towards the electrolyte. The concentration of the Al⁺ ions at the surface should increase proportionally with the anodic current density, so also the flux through the oxide and consequently the rate at which hydrogen evolves as the reaction product between Al⁺ ions and H₂O molecules (Eq. 3). The above phenomena contribute to adsorption of chloride ions at the oxide surface, penetration of the oxide film by chloride ions, and Cl[−]-assisted dissolution which occurs beneath the oxide film at the metal/oxide interface [5, 11, 33].

The two other models mentioned earlier cannot be readily associated with the experimentally established constancy of the NDE, i.e. the linear dependence of hydrogen evolution rate on anodic current density. This could be because the breakdown of a protective film and subsequent disintegration of the metal surface are likely to be stochastic processes, affected by factors not related to the mechanism of the reaction (i.e. mechanical stress created in the surface) [5]. These processes would likely lack reproducibility and could hardly be expected to render the above-mentioned linearity.

The impurities in the technical grade Al accelerate the H⁺ discharge reaction hence higher hydrogen evolution rates, i.e. larger negative difference effect as compared to the pure Al. The major impurity in technical grade Al is iron, which has very low solid solubility in the Al-matrix (of about 0.04 wt% at 665 °C) and is predominantly present in aluminium microstructure as intermetallic particles [34]. These iron-rich intermetallic particles are electrochemically nobler with respect to the remainder of the aluminium microstructure and function as small local cathodes [35–37].

The addition of alloying components, i.e. In and/or Sn to aluminium significantly alter the behaviour of technical grade aluminium under the same galvanostatic conditions. It is interesting to note that the potentials of galvanostatically polarized aluminium alloys in NaCl solution (Figs. 1, 2) are more negative than the equilibrium potential for H⁺/H₂ in the solution. This indicates that cathodic hydrogen evolution reaction can occur in the studied anodic current density range.

Due to low solubility of In and Sn in solid Al, the total quantity of alloying elements above the solubility limit at a determined temperature is segregated into inclusions predominantly not only at grain boundaries but also within metal grains [15, 38–41]. As a result, the distribution and morphology of segregated phases can be considered as the main characteristics affecting the electrochemical behaviour of Al-based alloys components. Previous studies suggest that the indium-enriched phases in the Al–In alloy act as cathodes and promote dissolution of the Al-matrix as well as increase the overpotential for the hydrogen evolution reaction [26, 42, 43]. Al–In alloy exhibits the lowest hydrogen evolution rate and NDE compared with the other examined alloys, indicating an inhibiting effect of indium on the hydrogen evolution reaction on aluminium [26, 42, 43]. On the other hand, Al–Sn alloy exhibits the highest hydrogen evolution rate and NDE compared with the other alloys, which supports the theory that tin is a much better catalyst for H₂ evolution than aluminium and it is to be expected that the tin inclusions will act as cathodic centres during the anodic dissolution reaction [15–17, 44, 45].

Results of hydrogen evolution rate and NDE for Al–In–Sn alloy can be explained from point of view of

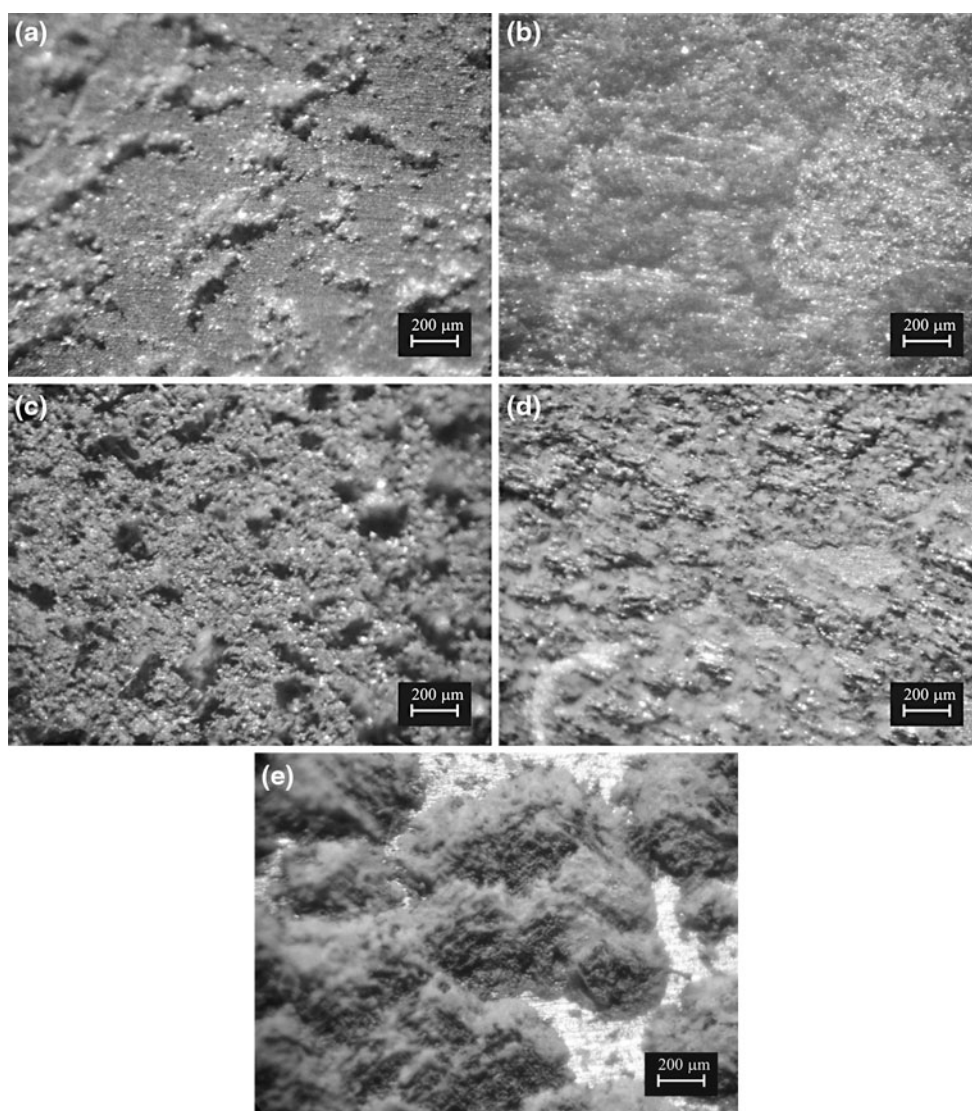


Fig. 5 Optical micrographs of the surface of **a** Al(5N), **b** Al(tech.), **c** Al-In, **d** Al-Sn, and **e** Al-In-Sn alloys after galvanostatic anodic polarization at 100 mA cm^{-2} in 2 mol dm^{-3} NaCl solution

microgalvanic corrosion. As demonstrated in our previous study [16], the low solubility of In and Sn in solid Al, during the preparation of Al-In-Sn alloy creates a possibility of extraction of both alloying elements mainly at grain boundaries. Contact between indium and tin could also lead to the formation of additional micro-galvanic cells in which indium acts as the anode with respect to tin. During anodic polarization of Al-In-Sn alloy in the chloride solution the dissolution of Al-In-Sn alloy introduces both aluminium and indium ions into the solution. The anodic reactions are accompanied by pronounced evolution of hydrogen, which takes place on the top of the Sn inclusions. However, the indium species may redeposit on the cathodic sites on the surface. The exchange current density for the hydrogen evolution reaction on the In is smaller than that on Al and Sn, therefore the In

deposition contributes to diminish the hydrogen evolution rate [26, 43].

3.1.1 Optical microscopy

After anodic polarization the different aluminium specimens were imaged using a light microscope (Fig. 5). The first visible sign of corrosion was the formation of small hydrogen bubbles on the surface of the metal. With increase in anodic polarization, the materials lost their reflective surfaces and subsequent extensive damage ensued. In this condition, the surface of pure and technical grade aluminium showed the effects of strong general dissolution (Fig. 5a, b).

For Al-In alloy at the lower anodic current density the surface showed irregularly shaped cavities, i.e. pitting corrosion. The images reveal 'bright' areas, distributed over

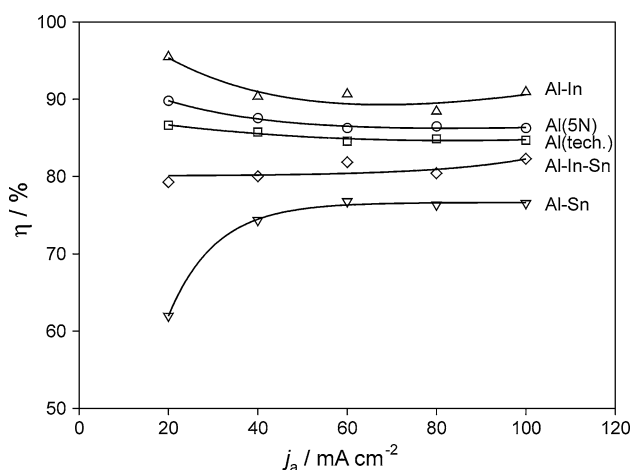


Fig. 6 Anode efficiency of Al(5N), Al(tech.), Al-In, Al-Sn and Al-In-Sn alloys at different anodic current densities in 2 mol dm⁻³ NaCl solution

the whole surface, which is probably indicative of the presence of indium in the alloy [38, 42, 46]. With increasing anodic polarization, the alloy surface exhibited a rough morphology that is consistent with strong general dissolution (Fig. 5c). General dissolution was also observed in the case of Al-Sn alloy, resulting in a rough surface with metallic luster (Fig. 5d). The Al-In-Sn alloy, manifested extensive surface damage and pitting after anodic polarization at 20 mA cm⁻². The number and size of the pits increased with the increase in the anodic current density. Hence, after the anodic current maximum had been applied the surface morphology was consistent with general dissolution (Fig. 5e). The apparent general dissolution characteristic of the activated specimens represents a positive feature for anode materials used in Al/air battery applications. The results clearly confirm that the examined aluminium alloys are likely to be suitable anodes for an Al/air battery with a sodium chloride electrolyte.

3.1.2 Anode efficiency

The anode efficiency (η) is defined as [7];

$$\eta(\%) = \frac{j}{j + j_{H_2}} \times 100 \quad (5)$$

where j is the impressed current and j_{H_2} the rate of hydrogen evolution. The calculated values of the anode efficiency are presented in Fig. 6. An increase in anodic current density leads to decrease in the anode efficiency of Al(5N) and Al(tech.). Again, it can be seen that the anode efficiency of the technical grade aluminium is only very slightly lower than that of pure aluminium, which means that it could be considered for use as anode material in Al/air batteries. As has been stated by de Souza and

Vielstich [47] the high-energy cost of Al(5N) reduces the overall thermodynamic efficiency of the battery to about 10 % (taking into account the Faradaic efficiency of dissolution, aluminium extraction and aluminium refining). According to the same authors, to reduce considerably the cost of the battery, high-purity smelter-grade (99.8 %) anodes should be used instead of pure ones [47, 48]. The anode efficiency of the Al-Sn as well as Al-In-Sn alloy increased in the range of the applied current density and at 100 mA cm⁻² reached 76.5 and 82.3 %, respectively. The Al-In alloy exhibits the highest anode efficiency among the alloys investigated, i.e. alloys derived from technical grade aluminium. Although the anode efficiency of Al-In alloy changed from 95.4 % at 20 mA cm⁻² to 92 % at 100 mA cm⁻², it is noteworthy that in the high-current region, for an aluminium/air cell in a typical operating range of current density, the anode efficiency increases. The performance of the tested electrodes on the basis of their anode efficiency is as follows: Al-In > Al(5N) > Al(tech.) > Al-In-Sn > Al-Sn. This means that the anode efficiency depends remarkably upon the composition of the alloys and hence will be closely related with the surface oxide film on aluminium. Accordingly, the alloying elements appear to affect not only the electrochemical properties of aluminium metal but also the properties and stability of the oxide film on aluminium [7]. Thus, the anode efficiency can be widely changed by alloying. The role of the minor elements indium and tin for the anode efficiency could be discussed in the terms of low solubility of the elements in aluminium, as mentioned earlier. The anodic behaviour of the alloys may be strongly influenced by the extent that the alloying elements are largely present in the alloys as small inclusions, i.e. as separate phases within the main aluminium structure [15, 38–41]. The presence of heterogeneities in the aluminium structure may also strongly affect the continuity and resistance of the oxide layer. Furthermore, the efficiency of the alloy is improved if the oxide film can easily be ruptured by chloride ions present in the electrolyte allowing the alloy to be available for future uniform dissolution [12].

4 Conclusions

In this article, we present the electrochemical characterization of five different electrodes including Al(5N), Al(tech.) and its alloys namely Al-In, Al-Sn, and Al-In-Sn as anode materials for aluminium/air batteries with sodium chloride electrolyte. The electrochemical results reveal that the addition of In and/or Sn as alloying components to aluminium reduces electrode polarization and that the corrosion of Al and its alloys is accompanied by strong hydrogen evolution at a rate that increases with

increasing the anodic polarization (NDE). Also, all the examined samples showed high-anode efficiency in the high-current density region, and with increasing anodic polarization, the surface of the tested alloys exhibited a rough morphology that is consistent with strong general dissolution.

The results show that each of the examined technical grade aluminium alloys is likely to be a suitable anode for an Al/air battery with sodium chloride electrolyte. Among the tested alloys, Al–In alloy was found to be the most promising since it exhibits a low anodic polarization, minimum hydrogen evolution rate, minimum NDE, a morphology which is consistent with general dissolution, and high-anode efficiency. In contrast Al–Sn and Al–In–Sn alloys showed higher hydrogen evolution rate.

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